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TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

6439

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/331818

INTERNATIONAL APPLICATION NO.  
PCT/US97/23771INTERNATIONAL FILING DATE  
23 December 1997PRIORITY DATE CLAIMED  
26 December 1996

TITLE OF INVENTION -- Laundry Detergent Compositions with Cellulosic Polymers to Provide Appearance and Integrity Benefits to Fabrics Laundered Therewith

APPLICANT(S) FOR DO/EO/US

WANG, Jiping; WASHINGTON, Nodie Monroe; HUNTER, Kathleen Brenner; BOYER, Stanton Lane

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application was filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☒ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

"Express Mail" mailing label number

EL174/0084845

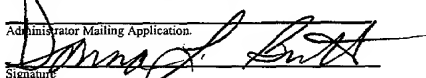
Date of Deposit

25 June 1999


I hereby certify that this paper/fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231

Administrator Mailing Application.

Signature



NOTED BY: 3430

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/US97/23771		ATTORNEY'S DOCKET NUMBER 6439	
				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$670	
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	10-20 =	0	x \$22.00	\$0	
Independent Claims	1-3 =	0	x \$78.00	\$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			\$250.00	\$0	
TOTAL OF ABOVE CALCULATIONS =				\$670	
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0	
TOTAL NATIONAL FEE =				\$670	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				\$0	
TOTAL FEES ENCLOSED =				\$670	
				Amount to be refunded	\$
				charged	\$
<p>a. [ ] A check in the amount of \$ ____ to cover the above fees is enclosed.</p> <p>b. [ x ] Please charge my Deposit Account No. <u>16-2480</u> in the amount of \$ <u>670</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. [ x ] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>16-2480</u> . A duplicate copy of this sheet is enclosed.</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO:</p>					
S.R. Chuey Patent Division The Procter & Gamble Company Ivorydale Technical Center 5299 Spring Grove Avenue Cincinnati, OH 45217				 Signature T. David Reed Name <u>32,931</u> Registration Number	

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of

U. S. National Phase Entry  
Under 35 USC 371 from  
the International Application of  
WANG, Jiping et al  
Int'l Application No. PCT/US97/23771  
Filed in the RO/US on 23 December 1997  
Entitled: Laundry Detergent Compositions with  
Cellulosic Polymers to Provide  
Appearance and Integrity Benefits to  
Fabrics Laundered Therewith

: "Express Mail" mailing label number EL17410084845: Date of Deposit: 25 June 1999: I hereby certify that this paper and/or fee is being  
: deposited with the United States Postal Service "Express  
: Mail Post Office to Addressee" service under 37 CFR 1.10  
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: Commissioner for Patents and Trademarks, Washington,  
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: Name

: Signature

## ASSOCIATE POWER OF ATTORNEY

Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

Dear Sir:


You are requested to recognize S. R. Chuey (Registration No. 39,140); B. M. Bolam (Registration No. 37,513); and K. W. Zerby (Registration No. 32,323) of The Procter & Gamble Company, Cincinnati, Ohio, and R. J. Snyder (Registration No. 31,062) and H. D. Kozlowski (Registration No. 30,468) of Dinsmore & Shohl, as Associate Attorney to prosecute this application, to make alterations and amendments therein, and to transact all business in the Patent Office connected with the application or with the patent granted thereupon.

Please address all future communications to:

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Respectfully submitted for Applicants,

By

  
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LAUNDRY DETERGENT COMPOSITIONS WITH CELLULOSIC POLYMERS  
TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS  
LAUNDERED THEREWITH

TECHNICAL FIELD

The present invention relates to heavy duty laundry detergent compositions, in either liquid or granular form, which contain certain types of modified cellulose ether materials to impart appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

BACKGROUND OF THE INVENTION

It is, of course, well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye from fabrics and textiles

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and impart a faded, worn out appearance as a result of diminished color intensity, and in many cases, as a result of changes in hues or shades of color.

Given the foregoing, there is clearly an ongoing need to identify materials which could be added to laundry detergent products that would associate themselves with the fibers of the fabrics and textiles laundered using such detergent products and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance. Any such detergent product additive material should, of course, be able to benefit fabric appearance and integrity without unduly interfering with the ability of the laundry detergent to perform its fabric cleaning function. The present invention is directed to detergent compositions containing certain types of cellulosic materials that perform in this desired manner.

### **SUMMARY OF THE INVENTION**

The laundry detergent compositions herein comprise from about 1% to 80% by weight of a deterative surfactant, from about 0.1% to 80% by weight of an organic or inorganic detergency builder and from about 0.1% to 8% by weight of certain types of modified cellulose ether fabric treatment agents. The deterative surfactant and detergency builder materials can be any of those useful in conventional laundry detergent products. The modified cellulose ether materials are those which have a molecular weight of from about 10,000 to 2,000,000 and are comprised of repeating substituted anhydroglucose units corresponding to the general Structural Formulas Nos. I, II and III set forth hereinafter in the "Detailed Description of the Invention" section. (In the Structural Formulas hereinafter set forth, substituents are shown in specific positions on the anhydroglucose rings which repeat to form the substituted cellulose ether polymers. It should be understood that this is for illustration purposes only and that such substituents may be found on any of the carbon atoms of the anhydroglucose rings.)

One useful type of cellulose ethers comprises hydrophobically-modified, nonionic materials with anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. Ring substituents are alkoxyated in amounts ranging from about 1 to 20 moles.

A second useful type of cellulose ether comprises cationic cellulose ether materials which may have anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. Anhydroglucose ring substituents

contain from about 1 to 20 moles of alkoxylation and from about 0.005 to 0.5 moles of quaternary ammonium cationic moieties.

A third type of cellulose ether comprises anionic cellulose ether materials which may have anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. The anhydroglucose rings in such anionic materials also have a degree of carboxymethyl substitution ranging from about 0.05 to 2.5. Combinations of the nonionic, cationic and anionic modified cellulose ethers can also be employed.

In its method aspect, the present invention relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions described herein, or formed from the individual components of such compositions. Laundering of fabrics and textiles in such washing solutions, followed by rinsing and drying, imparts fabric appearance benefits to the fabric and textile articles so treated. Such benefits can include improved overall appearance, pill/fuzz reduction, antifading, improved abrasion resistance, and/or enhanced softness.

#### **DETAILED DESCRIPTION OF THE INVENTION**

As noted, the laundry detergent compositions of the present invention essentially contain deterative surfactant, detergent builder and certain modified cellulose ether fabric treatment agents which serve to enhance fabric appearance and integrity upon use of the detergent compositions to launder fabrics and textiles. Each of these essential detergent composition components, as well as optional ingredients for such compositions and methods of using such compositions, are described in detail as follows: All percentages and ratios given are by weight unless other specified.

##### **A) Deterative Surfactant**

The detergent compositions herein essentially comprise from about 1% to 80% by weight of a deterative surfactant. Preferably such compositions comprise from about 5% to 50% by weight of this surfactant. Deterative surfactants utilized can be of the anionic, nonionic, zwitterionic, ampholytic or cationic type or can comprise compatible mixtures of these types. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905,

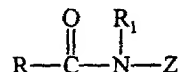
Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference. Of all the surfactants, anionics and nonionics are preferred.

Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional non-soap anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, and ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are a) the sodium, potassium and ammonium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-C<sub>18</sub> carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ammonium alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C<sub>11-13</sub> LAS.

Preferred nonionic surfactants are those of the formula  $R^1(OC_2H_4)_nOH$ , wherein  $R^1$  is a C<sub>10</sub>-C<sub>16</sub> alkyl group or a C<sub>8</sub>-C<sub>12</sub> alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C<sub>12</sub>-C<sub>15</sub> alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C<sub>12</sub>-C<sub>13</sub> alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:



wherein R is a C<sub>9-17</sub> alkyl or alkenyl, R<sub>1</sub> is a methyl group and Z is glycityl derived from a reduced sugar or alkoxyated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

#### B) Detergent Builder

The detergent compositions herein also essentially comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and



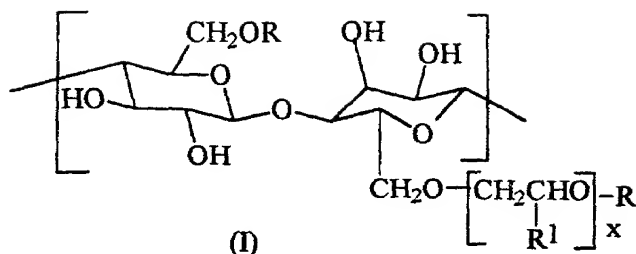
silicates having a weight ratio of  $\text{SiO}_2$  to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al, U. S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also, crystalline layered silicates such as those discussed in Corkill et al, U. S. Patent No. 4,605,509, incorporated herein by reference, are suitable for use in the detergent compositions of this invention.

### C) Modified Cellulosic Polymers

The third essential component of the detergent compositions herein comprises one or more modified cellulosic polymers. Such materials have been found to impart a number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such modified cellulosic materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, etc. The modified cellulosic polymers used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

The modified cellulosic polymers useful herein may be of the nonionic, cationic or anionic types, or the modified cellulosic polymeric component of the compositions herein may comprise combinations of these cellulosic polymer types. The modified cellulosic polymer component of the compositions herein will generally comprise from about 0.1% to 8% by the weight of the composition. More preferably, such modified cellulosic materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%.

One suitable type of modified cellulosic polymer for use herein comprises hydrophobically-modified, nonionic cellulose ethers having a molecular weight of from about 10,000 to 2,000,000, preferably from about 50,000 to 1,000,000. The hydrophobically-modified nonionic materials have repeating, substituted anhydroglucose units which correspond to the general Structural Formula No. I as follows:

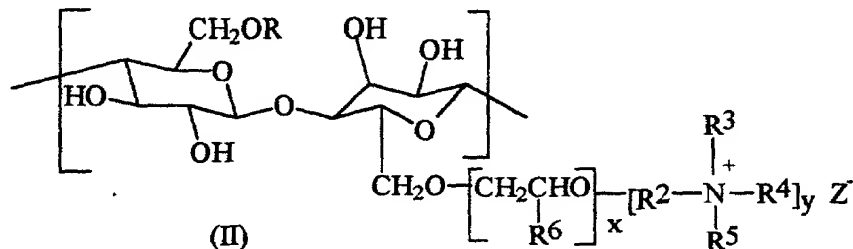


Structural Formula No. I

In Structural Formula No. I, R is a combination of H and C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. Alkyl substitution on the anhydroglucose rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymer material. Also, in Structural Formula No. I, R<sup>1</sup> is H or methyl, and x ranges from about 1 to 20, preferably from about 1 to 10.

The hydrophobically-modified nonionic cellulose ethers of Structural Formula No. I include those which are commercially available and also include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. I type include Polysurf 67, Natrosol Plus 430 and Natrosol Plus 330, all marketed by Hercules, Inc.

Another suitable type of modified cellulosic polymer for use herein comprises certain cationic cellulose ethers, which may or may not be hydrophobically-modified, having a molecular weight of from about 10,000 to 2,000,000, more preferably from about 10,000 to 1,000,000. These cationic materials have repeating substituted anhydroglucose units which correspond to the general Structural Formula No. II as follows:

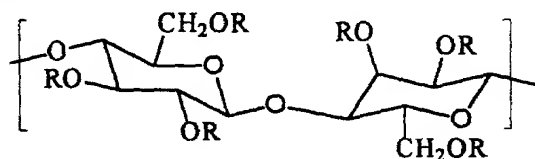


Structural Formula No. II

In Structural Formula No. II, R is H or C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. Alkyl substitution on the anhydroglucose rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymeric material. Also, in Structural Formula No. II, R<sup>2</sup> is CH<sub>2</sub>CHOHCH<sub>2</sub> or C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently methyl, ethyl or phenyl. R<sup>6</sup> is H or methyl. Further, in Structural Formula No. II, x ranges from about 1 to 20, preferably from about 1 to 10; and y ranges from about 0.005 to 0.5, preferably from about 0.005 to 0.1; and Z is Cl<sup>-</sup> or Br<sup>-</sup>.

The cationic cellulose ethers of Structural Formula No. II likewise include those which are commercially available and further include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. II type include the JR 30M, JR 400, JR 125, LR 400 and LK 400 UCARE polymers, all marketed by Union Carbide Corporation.

A third type of suitable modified cellulose polymers for use herein comprises certain anionic cellulose ethers, which also may or may not be hydrophobically-modified, having a molecular weight of from about 10,000 to 2,000,000, more preferably from about 50,000 to 1,000,000. These anionic materials have repeating substituted anhydroglucose units which correspond to general Structural Formula No. III as follows:

Structural Formula No. III

In Structural Formula No. III, R is a combination of H and a) CH<sub>2</sub>COOA and, optionally, b) C<sub>2</sub>-C<sub>24</sub>, preferably C<sub>2</sub> - C<sub>16</sub>, alkyl, with A being Na or K. Alkyl substitution on the anhydroglucose rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymer material. The anionic cellulose ethers also have a degree of carboxymethyl

substitution which ranges from about 0.05 to 2.5, more preferably from about 0.1 to 1.0.

The anionic cellulose ethers of Structural Formula No. III also include those materials which are commercially available and further include those which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. III include CMC 7H, CMC 99-7M and CMC 99-7L, all marketed by Hercules, Inc. and CMC D72, CMC D65 and CMC DHT, all marketed by Penn Carbose.

The commercially available cellulose ether materials useful herein are themselves derived from suitable natural sources of cellulose. Such sources include, for example, cotton linters and other vegetable tissues. The modified cellulose ethers used in this invention are generally all water-soluble materials. They can therefore be utilized for detergent composition preparation in the form of aqueous solutions of the such cellulosic polymers if desired.

#### D) Optional Detergent Ingredients

In addition to the essential surfactants, builders and modified cellose ethers hereinbefore described, the detergent composition of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as bleaches and bleach activators, enzymes and enzyme stabilizing agents, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, organic and inorganic fillers, solvents, hydrotropes, optical brighteners, dyes and perfumes.

A preferred optional ingredients for incorporation into the detergent compositions herein comprises a bleaching agent, e.g., a peroxygen bleach. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

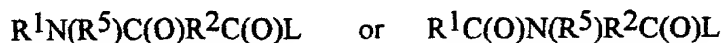
Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published

February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used, generally in particulate form, in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials. For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interlox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical and preferred. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

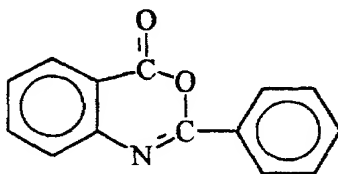
Other useful amido-derived bleach activators are those of the formulae:



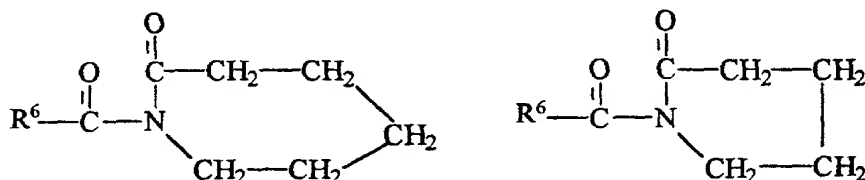
wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein  $R^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, nonanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If utilized, peroxygen bleaching agent will generally comprise from about 2% to 30% by weight of the detergent compositions herein. More preferably, peroxygen bleaching agent will comprise from about 2% to 20% by weight of the compositions. Most preferably, peroxygen bleaching agent will be present to the extent of from about 3% to 15% by weight of the compositions herein. If utilized, bleach activators can comprise from about 2% to 10% by weight of the detergent compositions herein.

Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

Another highly preferred optional ingredient in the detergent compositions herein is a detergent enzymes component. Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases, amylases and peroxidases.

Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-

Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 10. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein.

The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a



manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

#### E) Detergent Composition Preparation

The detergent compositions according to the present invention can be in liquid, paste or granular forms. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients (e.g. surfactants, builders, water, etc.) as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients can be admixed in granular powder form with the spray dried granules in a rotary mixing drum and the liquid ingredients (e.g. organic solutions of the essential cellulosic polymers, enzymes, binders and perfumes) can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Addition of the cellulose ether component to liquid detergent compositions of this invention may be accomplished by simply mixing into the liquid detergent aqueous solutions of the desired cellulose ethers. Cellulose ethers can alter the viscosity or other rheological characteristics of liquid detergent products. It may

therefore be necessary to compensate for any rheological changes in the liquid detergent product brought about by cellulose ether addition by altering the type and amount of hydrotropes and/or solvents that are used.

#### F) Fabric Laundering Method

The present invention also provides a method for laundering fabrics in a manner which imparts fabric appearance benefits provided by the cellulosic polymers used herein. Such a method employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described or formed from the individual components of such compositions. Contacting of fabrics with washing solution will generally occur under conditions of agitation although the compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment.

Agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective amount of the liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 7000 ppm, more preferably from about 1000 to about 3000 ppm.

#### G) Fabric Conditioning

The modified cellulose ethers hereinbefore described as components of the laundry detergent compositions herein may also be used to treat and condition fabrics and textiles in the absence of the surfactant and builder components of the detergent composition embodiments of this invention. Thus, for example, a fabric conditioning composition comprising only the modified cellulose ethers themselves, or comprising an aqueous solution of the modified cellulose ethers, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described.

### EXAMPLES

The following examples illustrate the compositions and methods of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

**EXAMPLE I****Liquid Detergent Test Composition Preparation**

Several heavy duty liquid detergent compositions are prepared containing various modified cellulosic polymers. Such liquid detergent compositions all have the following basic formula:

**Table A**

<b><u>Component</u></b>	<b><u>Wt. %</u></b>
C <sub>12-15</sub> alkyl ether (2.5) sulfate	38
C <sub>12</sub> glucose amide	6.86
Citric Acid	4.75
C <sub>12-14</sub> Fatty Acid	2.00
Enzymes	1.02
MEA	1.0
Propanediol	0.36
Borax	6.58
Dispersant	1.48
Na Toluene Sulfonate	6.25
Modified Cellulosic Polymer (if present)	2.0
Dye, Perfume, Brighteners, Preservatives, Suds Suppressor, Other Minors, Water	<b><u>Balance</u></b>
	100%

**EXAMPLE II****Granular Detergent Test Composition Preparation**

Several heavy duty granular detergent compositions are prepared containing various modified cellulosic polymers. Such granular detergent compositions all have the following basic formula:

**Table B**

<u>Component</u>	<u>Wt. %</u>
C <sub>12</sub> Linear alkyl benzene sulfonate	9.31
C <sub>14-15</sub> alkyl ether (0.35 EO) sulfate	12.74
Zeolite Builder	27.79
Sodium Carbonate	27.31
PEG 4000	1.60
Dispersant	2.26
C <sub>12-13</sub> Alcohol Ethoxylate (9 EO)	1.5
Sodium Perborate	1.03
Soil Release Polymer	0.41
Enzymes	0.59
Modified Cellulosic Polymer (if present)	2.5
Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate	<u>Balance</u>
	100%

**EXAMPLE III****Cellulosic Polymers Used in Test Compositions**

The representative modified cellulosic polymers used in the liquid and granular detergent compositions described in Examples I and II are characterized in Table C. The various substituents listed are those from Structural Formulas Nos. I, II and III described hereinbefore.

Table C  
Cellulosic Polymers Used in Test Detergent Compositions

<u>Polymer Description</u>	<u>Polymer ID</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Polymer Tradename	Polysurf 67	LK-400	CMC (D72)	Modified LK-400
Polymer Manufacturer	Hercules	Union Carbide	Penn Carbose	Union Carbide
Polymer Type	Nonionic	Cationic	Anionic	Cationic
Molecular Weight	700-750M	~400M	~300M	~400M
Structure No.	I	II	III	II
R	Cetyl (C <sub>16</sub> )	H	CH <sub>2</sub> COO A	H
Amount of Ring Alkyl Substitution	0.4%- 0.6%	0	0	0
Degree of Ring Carboxymethyl Substitution	-	-	0.5	-
R <sup>1</sup>	H	-	-	-
R <sup>2</sup>	-	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> -	-	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> -
R <sup>3</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>4</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>5</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>6</sup>	-	H	-	H
x	1-3	1-3	-	1-3
y	-	~0.1	-	~0.006
Z	-	Cl <sup>-</sup>	-	Cl <sup>-</sup>
A	-	-	Na	-

Test compositions prepared as described in Examples I and II are evaluated for the effects that the various cellulosic polymers of Example III provide when samples of fabrics or garments are washed using the test compositions as described, all under identical conditions. A control sample with no polymer is usually compared to one composition with a test polymer to be evaluated. Testing conditions are also carefully monitored. Examples of controlled conditions include: wash time, wash

water temperature and hardness; washer agitation; rinse time, rinse water temperature and hardness; dryer time and temperature; wash load fiber content and weight.

#### **EXAMPLE IV**

##### **Overall Appearance**

In an **Overall Appearance** test, fabrics are washed using various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed after ten cycles are then comparatively graded by three judges who evaluate the overall appearance of the washed fabrics. It is the decision of the judge as to what is to be evaluated unless specific direction is given to evaluate one attribute such as color, pilling, fuzz, etc.

In the **Overall Appearance** test, the visual preference of the judge is expressed using the Scheff scale.

That is:

- 0 = No difference
- 1 = I **think** this one is better (unsure).
- 2 = I **know** this one is a **little** better.
- 3 = I know this one is a **lot** better.
- 4 = I know this one is a **whole lot** better.

For the **Overall Appearance** test, laundering conditions are as follows:

Washer Type: Kenmore (17 gallons)

Wash Time: 12 min

Wash Temperature: 90°F (32.2°C)

Wash Water Hardness: 6 grains per gallon

Washer Agitation: normal

Rinse Time: 2 min

Rinse Temperature: 60°F (15.6°C)

Rinse Water Hardness: 6 grains per gallon

Wash Load Fabric Content: various colored and white garments and  
fabrics

Wash Load Weight: 5.5 lbs (2.5 kg)

The average overall appearance test results are shown in Tables D and E.

Table DOverall Appearance Test Results

<u>Liquid Test Composition ID</u>	<u>Polymer Tested</u>	<u>Overall Appearance Grade</u>
Control	None	0
A	Polysurf 67	1.5
B	LK-400	1.8
C	CMC (D72)	1.0
D	Modified LK-400	1.2

Table EOverall Appearance Test Results

<u>Granular Test Composition ID</u>	<u>Polymer Tested</u>	<u>Overall Appearance Grade</u>
Control	None	0
A	Polysurf 67	1.4
B	LK-400	1.0
C	CMC (D72)	1.0
D	Modified LK-400	1.1

EXAMPLE VPill Reduction

In a **Pill Reduction** test, fabrics are washed using the various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed are then graded for Pill Reduction using a computer-assisted pilling image analysis system which employs image analysis to measure the number of pills on tested garments and fabrics. Pill reduction is calculated as:

$$\text{Pill reduction(\%)} = \{ [\# \text{ pills (control)} - \# \text{ pills (polymers)}] / \# \text{ pills (control)} \} \times 100\%$$

For the Pill Reduction test, laundering conditions are the same as used for the Overall Appearance test described hereinbefore in Example IV.

The average % Pill Reduction test results are shown in Tables F and G.

**Table F**  
**Pill Reduction Test Results - Liquids**

<u>Liquid Test Composition ID</u>	<u>Polymer Tested</u>	<u>Pill/Fuzz Reduction (%)</u>
Control	None	0
A	Polysurf 67	21.5
B	LK-400	42.4
C	CMC(D72)	26.8
D	Modified LK-400	25.9

**Table G**  
**Pill Reduction Test Results - Granular**

<u>Granular Test Composition</u>	<u>Polymer Tested</u>	<u>Pill/Fuzz Reduction (%)</u>
<u>ID</u>		
Control	None	
A	Polysurf 67	33.3
B	LK-400	51.6
C	CMC(D72)	7.6
D	Modified LK-400	16.6



**EXAMPLE VI****Color Protection**

In a **Color Protection** test, fabrics are washed using various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed are then tested with a Hunter colorimeter in order to determine a Delta E\* value for each fabric tested. Delta E\* is defined as the color difference (reflectance intensity, hue shift, etc.) between washed fabrics and unwashed fabrics.

For the Color Protection test, laundering conditions are the same as used for the Overall Appearance test described hereinbefore in Example IV.

The extent of **Color Protection** provided is based on percent of Delta E\* difference compared to an unwashed sample. Color protection is calculated as:

$$\% \text{ Color Protection} = \{ [dE^*(\text{control}) - dE^*(\text{polymers})] / dE^*(\text{control}) \} \times 100\%$$

The average color protection test results are shown in Tables H and I.

**Table H**

**Color Protection Test Results - Liquids**

<u>Liquid Test Composition ID</u>	<u>Polymer Tested</u>	<u>Color Protection (%)</u>
Control	None	0
A	Polysurf 67	24.2
B	LK-400	36.5
C	CMC (D72)	26.6
D	Modified LK-400	27.2

Table I  
Color Protection Test Results - Granular

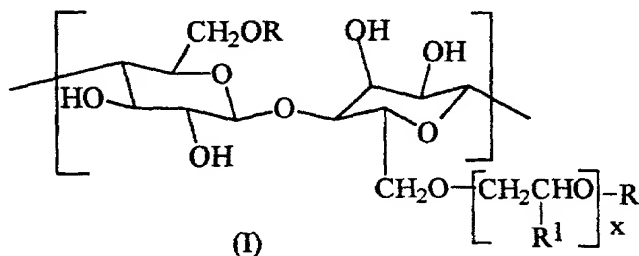
<u>Granular Test Composition</u>	<u>Polymer Tested</u>	<u>Color Protection (%)</u>
<u>ID</u>		
Control	None	0
A	Polysurf 67	33.9
B	LK-400	39.2
C	CMC (D72)	15.5
D	Modified LK-400	24.7

Year	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100																			
Population	1,000,000	1,050,000	1,100,000	1,150,000	1,200,000	1,250,000	1,300,000	1,350,000	1,400,000	1,450,000	1,500,000	1,550,000	1,600,000	1,650,000	1,700,000	1,750,000	1,800,000	1,850,000	1,900,000	1,950,000	2,000,000	2,050,000	2,100,000	2,150,000	2,200,000	2,250,000	2,300,000	2,350,000	2,400,000	2,450,000	2,500,000	2,550,000	2,600,000	2,650,000	2,700,000	2,750,000	2,800,000	2,850,000	2,900,000	2,950,000	3,000,000	3,050,000	3,100,000	3,150,000	3,200,000	3,250,000	3,300,000	3,350,000	3,400,000	3,450,000	3,500,000	3,550,000	3,600,000	3,650,000	3,700,000	3,750,000	3,800,000	3,850,000	3,900,000	3,950,000	4,000,000	4,050,000	4,100,000	4,150,000	4,200,000	4,250,000	4,300,000	4,350,000	4,400,000	4,450,000	4,500,000	4,550,000	4,600,000	4,650,000	4,700,000	4,750,000	4,800,000	4,850,000	4,900,000	4,950,000	5,000,000	5,050,000	5,100,000	5,150,000	5,200,000	5,250,000	5,300,000	5,350,000	5,400,000	5,450,000	5,500,000	5,550,000	5,600,000	5,650,000	5,700,000	5,750,000	5,800,000	5,850,000	5,900,000	5,950,000	6,000,000	6,050,000	6,100,000	6,150,000	6,200,000	6,250,000	6,300,000	6,350,000	6,400,000	6,450,000	6,500,000	6,550,000	6,600,000	6,650,000	6,700,000	6,750,000	6,800,000	6,850,000	6,900,000	6,950,000	7,000,000	7,050,000	7,100,000	7,150,000	7,200,000	7,250,000	7,300,000	7,350,000	7,400,000	7,450,000	7,500,000	7,550,000	7,600,000	7,650,000	7,700,000	7,750,000	7,800,000	7,850,000	7,900,000	7,950,000	8,000,000	8,050,000	8,100,000	8,150,000	8,200,000	8,250,000	8,300,000	8,350,000	8,400,000	8,450,000	8,500,000	8,550,000	8,600,000	8,650,000	8,700,000	8,750,000	8,800,000	8,850,000	8,900,000	8,950,000	9,000,000	9,050,000	9,100,000	9,150,000	9,200,000	9,250,000	9,300,000	9,350,000	9,400,000	9,450,000

What is claimed is:

I. A laundry detergent composition which imparts fabric appearance benefits selected from pill/fuzz reduction, antifading, improved abrasion resistance and/or enhanced softness to fabrics and textiles laundered in aqueous washing solutions formed therefrom, which composition is characterized by:

- A) from 1% to 80% by weight of a deterative surfactant;
- B) from 0.1% to 80% by weight of an organic or inorganic detergency builder;
- C) from 0.1% to 8% by weight of a modified cellulose ether fabric treatment agent selected from the group consisting of:
  - i) hydrophobically-modified, nonionic cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:



wherein:

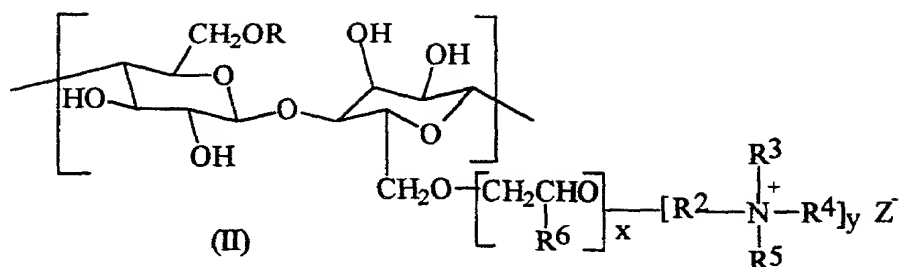
R is a combination of H and C<sub>8</sub>-C<sub>24</sub> with alkyl substitution of the anhydroglucose rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material;

R<sup>1</sup> is H or methyl; and

x ranges from 1 to 20;

- ii) cationic quaternary ammonium cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:

25



wherein:

R is H or C<sub>8-24</sub>, with alkyl substitution of the anhydroglucose rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material;

R<sub>2</sub> is CH<sub>2</sub>CHOHCH<sub>2</sub> or C<sub>8-24</sub> alkyl;

R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each, independently, methyl, ethyl or phenyl;

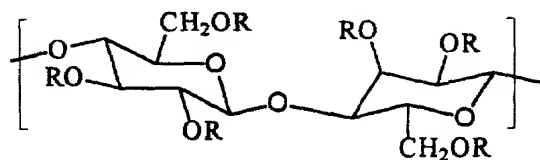
R<sub>6</sub> is H or methyl;

x ranges from 1 to 20;

y ranges from 0.005 to 0.5; and

Z is Cl<sup>-</sup> or Br<sup>-</sup>;

- iii) anionic cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:



(III)

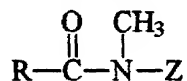
wherein:

R is a combination of H and a) CH<sub>2</sub>COOA, and, optionally, b) C<sub>8-24</sub> alkyl, with alkyl substitution of the anhydroglucose rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material, and with the degree of carboxymethyl substitution of the anhydroglucose rings ranging from 0.05 to 2.5; and wherein A is Na or K; and

- iv) combinations of said nonionic, cationic and anionic cellulose ethers.

2. A composition according to Claim 1 wherein
- A) the deterative surfactant comprises from 5% to 50% by weight and is selected from anionic and nonionic surfactant materials
  - B) the detergency builder is characterized by from 10% to 50% by weight and is selected from carboxylates, silicates, aluminosilicates, carbonates, borates and combinations thereof; and
  - C) the modified cellulose ether fabric treatment agents comprises from 0.5% to 4% by weight and have molecular weights ranging from 10,000 to 1,000,000.
3. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is a hydrophobically-modified, nonionic material corresponding to Structural Formula No. I wherein
- a) R is a combination of H and C<sub>8</sub> to C<sub>16</sub> alkyl;
  - b) R substitution of the anhydroglucose rings ranges from 0.2% to 2% by weight of the cellulose ether;
  - c) R<sup>1</sup> is H; and
  - d) x ranges from 1 to 10.
4. A composition according to Claim 3 wherein the hydrophobically-modified, nonionic cellulose ether is selected from Polysurf 67, Natrosol Plus 430 and Natrosol Plus 330.
5. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is a cationic material corresponding to Structural Formula No. II wherein
- a) R is C<sub>8</sub> to C<sub>16</sub> alkyl;
  - b) R substitution of the anhydroglucose rings ranges from 0.2% to 2% by weight of the cellulose ether;
  - c) R<sup>2</sup> is C<sub>8</sub> to C<sub>16</sub> alkyl or is CH<sub>2</sub>CH(OH)CH<sub>2</sub>;
  - d) R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each methyl;
  - e) R<sup>6</sup> is H;

- f) x ranges from 1 to 10;
  - g) y ranges from 0.005 to 0.1; and
  - h) Z is Cl<sup>-</sup>.
6. A composition according to Claim 5 wherein the cationic cellulose ether is selected from UCARE JR 30M, JR 400, JR 125, LR 400 and LK 400 and derivatives thereof.
  7. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is a anionic material corresponding to Structural Formula No. III wherein:
    - a) R is optionally C<sub>8</sub> to C<sub>16</sub> alkyl;
    - b) R substitution of the anhydroglucose rings ranges from 0.2% to 2% by weight of the cellulose ether;
    - c) the degree of carboxymethyl substitution ranges from 0.1 to 1.0; and
    - d) A is Na.
  8. A composition according to Claim 7 wherein the anionic cellulose ether is selected from CMC 7H, CMC 99-7M, CMC 99-7L, CMC D72, CMC D65 and CMC DHT.
  9. A composition according to Claim 2 in liquid form which is characterized by:
    - a) from 5% to 50% by weight of a deterative surfactant selected from
      - i) sodium, potassium and ammonium alkylsulfates wherein the alkyl group contains from 10 to 22 carbon atoms;
      - ii) sodium, potassium and ammonium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;
      - iii) polyhydroxy fatty acid amides of the formula



wherein R is a C<sub>9-17</sub> alkyl or alkenyl and Z is glycyl derived from a reduced sugar or alkoxylated derivatives thereof;

- iv) alcohol ethoxylates of the formula  $R^1(OC_2H_4)_nOH$  wherein  $R^1$  is a  $C_{10}$ - $C_{16}$  alkyl group or a  $C_8$ - $C_{12}$  alkyl phenyl group and  $n$  is from 3 to 80; and
  - v) combinations of these surfactants; and
  - b) from 1% to 10% by weight of a detergent builder component selected from carboxylate and polycarboxylate builders.
10. A composition according to Claim 2 in granular form which is characterized by:
- a) from 5% to 50% by weight of a deterative surfactant selected from
    - i) sodium and potassium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;
    - ii) sodium and potassium  $C_9$  to  $C_{15}$  alkyl benzene sulfonates;
    - iii) sodium and potassium  $C_8$  to  $C_{18}$  alkyl sulfates;
    - iv) polyhydroxy fatty acid amides of the formula
 
$$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \parallel \quad | \\ \text{R}-\text{C}-\text{N}-\text{Z} \end{array}$$
 wherein  $R$  is a  $C_9$ - $C_{17}$  alkyl or alkenyl and  $Z$  is glycyl derived from a reduced sugar or alkoxylated derivatives thereof; and
  - v) combinations of these surfactants; and
  - b) from 1% to 50% by weight of a detergent builder selected from sodium carbonate, sodium silicate, crystalline layered silicates, aluminosilicates, oxydisuccinates and citrates;

## DECLARATION COMBINED WITH POWER OF ATTORNEY

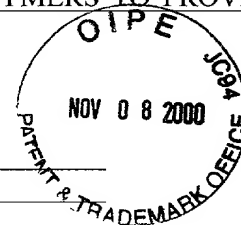
Page 1 of 2  
Attorney Docket No. 6439

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled LAUNDRY DETERGENT COMPOSITIONS WITH CELLULOSIC POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS LAUNDERED THEREWITH  
the specification of which

(check ☐ is attached hereto.  
one) ☒ was filed on December 23, 1997 as Application  
Serial No. PCT/US97/23771  
and was amended on \_\_\_\_\_  
(if applicable)



I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56.

I hereby claim foreign priority benefits under Title 35 United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.				
60/033,930		December 26, 1996		

Application Serial No.	Filing Date	Application Serial No.	Filing Date
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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (If applicable)

As named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Atty Name	Atty Reg Number	of Attorney Attached	
Kim William Zerby	32,323	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
Steven W. Miller	31,984	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
T. David Reed	32,931	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
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C. Brant Cook	39,151	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No
Marianne Dressman	42,498	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No

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The Procter &amp; Gamble Company

(513) 627-4132

Name

Phone No.

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Street

City

State

Zip Code



I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first joint inventor Jiping (nmn) Wang

Inventor's signature [Signature]

10/26/2000  
Date

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Citizenship ~~P.R. China~~ United States (JW)

Post Office Address 6546 Glenarbor Drive, West Chester, Ohio 45069

Full name of second joint inventor, if any Nodie Monroe Washington

Inventor's signature [Signature]

10/30/2001  
Date

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Citizenship United States

Post Office Address 1089 Wilberforce-Clifton Road, Wilberforce, Ohio 45384

Full name of third joint inventor, if any Kathleen Brenner Hunter

Inventor's signature \_\_\_\_\_

Date

Residence 2232 Amsterdam Road, Villa Hills, Kentucky 41017

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Full name of fourth joint inventor, if any Stanton Lane Boyer

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10/27/00

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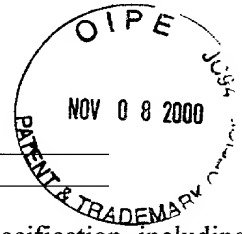
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